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16. ABSTRACT

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Influence of Algae on Photolysis Rates of Chemicals in Water

Richard G. Zepp* and Patricia F. Schlotzhauer

U.S. Environmental Protection Agency, Environmental Research Laboratory, Athens, Georgia 30613

■ Sunlight-induced algal transformations of 22 nonionic organic chemicals were studied in order to provide kinetic results and equations concerning the influence of algae on the behavior of pollutants in freshwater environments. Screening studies indicated that green and blue-green algae, at concentrations of 1–10 mg of chlorophyll *a*/L, accelerate photoreaction of certain polycylic aromatic hydrocarbons, organophosphorus compounds, and anilines in water. The rate of change in aniline concentration, [P], in the aniline–*Chlamydomonas* photoreaction can be described by the following expression: rate = $A(1 + B/[P])^{-1}$. At low substrate concentrations, the reaction rate is first order with respect to both algae and substrate concentration. Methyl parathion and parathion photoreacted 390 times more rapidly when sorbed by algae than in distilled water, and aniline and *m*-toluidine reacted over 12 000 times faster, indicating that light-induced algal transformations of certain pollutants may be significant. Other results indicated that reaction rates are unaffected by heat-killing the algae.

Introduction

The role of sunlight in the transport and transformation of chemicals in natural waters is affected in various ways by suspended particles such as sediments or microorganisms. These particles may influence photolysis rates of chemicals in water bodies through attenuation of sunlight (*1–3*), through initiation of indirect photoprocesses (*4–6*), and through physical or chemical interactions that change the microenvironment or alter the speciation of a photoreactive chemical.

Several recent studies have focused on the influence of sediments (*1, 2*) and algae (*3*) on the attenuation of solar radiation in natural waters. Other studies (*4–6*) have examined the photoreactivity of organic chemicals that are sorbed on suspended sediments.

The studies reported here concerning sunlight-induced transformation rates of nonionic organic chemicals involving algae were prompted by several considerations. First, bioaccumulation of a pollutant by algae is expected to be affected by the rate of degradation of the pollutant by the algae as well as by other factors such as the hydrophobicity of the pollutant (*7, 8*). Moreover, because algae are the most important sunlight absorbers in many aquatic environments (*3*), the algae-mediated phototransformation of toxic chemicals may have a significant effect on concentrations in the water column. To assess the significance of this process by using deterministic computer models (*9*), rates of transformations involving algae are required. A number of studies have shown that visible light absorption by the photosynthetic apparatus of algae commonly results in the photometabolism of polar, ionic organic substrates such as carboxylic acids, carbohydrates, and amino acids (*10*). Other investigations demonstrated that nonionic organic compounds, including pesticides, photolyze more rapidly in the presence of photosynthetic microorganisms (*11*). Most of these studies, however, were conducted in culture media by using artificial light sources having spectral outputs that are dissimilar to sunlight, especially in the photochemically important ultraviolet region.

In this report experimental results are presented concerning transformation rates of a broad cross section of chemicals in the presence of living algae and sunlight. The chemicals include polycyclic aromatic hydrocarbons, organophosphorus insecticides, anilines, phenol, and various other organic chemicals with structural features commonly found in commercial synthetic chemicals. Kinetic data are analyzed to formulate a rate expression and a kinetic model for the light-induced transformations. Finally, results concerning possible mechanisms for indirect photoreactions involving algae are presented.

Experimental Section

Chemicals. Aromatic hydrocarbons were purified as described by Zepp and Schlotzhauer (*12*). γ-Methoxy-*m*-(trifluoromethyl)butyrophenone (MTB) was synthesized as described elsewhere (*5*). *cis*-1,3-Pentadiene was obtained commercially and purified by distillation. *p*-Nitroacetophenone and *p*-nitroanisole (PNA) were also obtained commercially and were purified by recrystallization from 95% ethanol. Commercially obtained refer-

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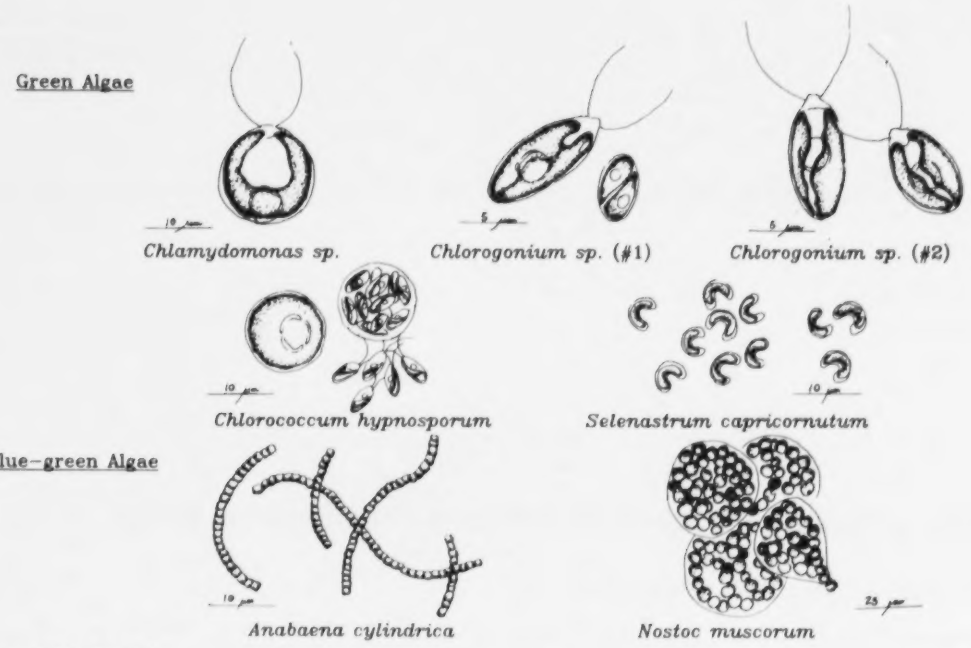


Figure 1. Algae used in the study.

ence standards of aniline, *m*-toluidine, *cis*-1,2-dichloroethylene, and nitrobenzene were used as received. The remaining chemicals were obtained from the U.S. Environmental Protection Agency, Research Triangle Park, NC, and were used as received.

Algae. Pure cultures of six algae commonly found in U.S. waters were obtained from the Starr collection at the University of Texas, Austin, TX, and from the Department of Botany, University of Georgia, Athens, GA (Figure 1). The identities of the algae were determined by microscopic examination. The algae were grown at 20 °C under Vitalites (TM) by using an 8:16 light–dark cycle. The growth medium (*13*) consisted of 0.005 M KNO_3, 0.0005 M K_2HPO_4, 0.0005 M KH_2PO_4, 0.002 M $MgSO_4$, 0.000 25 M $Ca(NO_3)_2$, 130 μM EDTA, 76 μM $ZnSO_4$, 180 μM H_3BO_3, 26 μM $MnCl_2$, 18 μM $FeSO_4$, 6.7 μM $CoCl_2$, 6.3 μM, $CuSO_4$, and 0.89 μM ammonium paramolybdate; the medium was adjusted to pH 5.5 by using hydrochloric acid. Algae used in most of the experiments were obtained from axenic cultures that were started every 10–14 days to keep the cells growing in log phase. For some experiments with aniline and methyl parathion, the algae were heat-killed by warming them to 50 °C for 30 min. To remove collodial ferric hydroxide particles that may have adsorbed on the cells, a modified version of the procedure described by Anderson and Morel (*14*) was used in some of the experiments with methyl parathion or aniline. This procedure involved washing the cells by gentle agitation for 30 min with 0.01 M aqueous ascorbic acid adjusted to pH 3.

General Procedures. With employment of centrifugation procedures that are discussed elsewhere (*5*), the majority of the chemicals that were studied were found to be sorbed less than 5% by the algae under the reaction conditions used. Analysis for these chemicals was accomplished by first centrifuging the algae suspensions (2500 rpm for 20 min) and then analyzing the supernatant with a Micromeritics high-pressure liquid chromatograph (HPLC) equipped with UV and fluorescence detectors. Direct aqueous injections were made onto an ODS-2 column, employing an acetonitrile–water mixture as mobile phase.

An alternative procedure was used in the case of the chemicals that were more strongly sorbed to the algae. These chemicals included pyrene, phenanthrene, fluoranthene, aldrin, Ronnel, and chlorpyrifos. This procedure involved exhaustive extraction of the algae suspension by an organic solvent after addition of 35% acetonitrile, by volume. The organic layer was analyzed by HPLC using a silica gel column with isooctane–isopropyl alcohol as mobile phase or by gas–liquid chromatography (GLC) employing a Tracor MT-222 gas chromatograph equipped with a linearized ^{63}Ni electron capture detector. The GLC columns were packed with 3% SE-30 or with 1.5% OV-17 and 1.95% OV-210 on 80/100 Gas Chrom Q. With methyl parathion and aniline, two compounds that were sorbed less than 5% on the algae, equivalent results were obtained when this extraction procedure was compared to the usual procedure involving direct analysis of the supernatant.

The volatile chemicals pentadiene and dichloroethylene were studied in air-saturated algae suspensions contained in gas-tight reaction cells that were filled to eliminate head space. After light exposure, a portion of the reaction-cell contents were removed, and the head space was analyzed by GLC employing a 6-m long by 2-mm i.d. column packed with 20% 1,2,3-tris(2-cyanoethoxy)propane on Gas Chrom RA (*15*).

Chlorophyll *a* concentrations were determined as described elsewhere (*16*), and the procedure of Houle et al. (*17*) was used to analyze for formaldehyde.

Screening Procedures. After washing the algae three times with distilled water, the cells were suspended in an aqueous solution having a substrate concentration that was lower than 2.0×10^{-5} M and lower than the solubility limit of the substrate. The resulting algae suspensions along with solutions of the substrate in distilled water were exposed to sunlight in test tubes that were mounted on a rotating, tilted turntable (a Cole-Palmer Roto-Torque heavy duty rotator) to provide the mixing necessary to maintain uniform suspensions. Solutions of PNA (1.0×10^{-5} M) were also exposed to sunlight on the turntable along with the algae suspensions and the distilled water solutions. After exposure for time t (usually 3–4 h), rate

Table I. Effects of Several Algae (1–10 mg/L Chlorophyll *a*) on Sunlight-Induced Transformation Rate Constants, $(k_p)_p/(k_p)_{act}$, of Selected Organic Chemicals[a]

compound	distilled water	*Chlamydomonas* sp.	*Chlorogonium* sp. (1)	*Chlorogonium* sp. (2)	*Chlorococcum hypnosporum*	*Selenastrum capricornutum*	*Anabaena cylindrica*
pyrene	5.4	9.5 (1.8)	6.3 (1.2)		12 (2.2)	6.0 (1.1)	4.6 (0.84)
phenanthrene	0.67	0.38 (0.57)	0.21 (0.31)	0.16 (0.24)	0.52 (0.77)	1.6 (2.4)	0.13 (0.19)
fluoranthene	0.14	0.92 (6.6)	1.5 (10)	1.0 (7.3)	1.1 (7.9)		1.6 (11)
naphthalene	0.055	0.15 (2.7)	0.11 (2.0)		0.12 (2.2)	0.12 (2.2)	0.07 (1.3)
aniline	0.04	2.0 (50)	0.41 (10)	0.28 (7)	0.31 (8)	0.15 (4)	0.86 (20)
phenol	<0.02	0.11	0.04			<0.04	0.04
aldrin		1.8	1.0	0.855	0.41	0.30	2.1
cis-1,2-dichloroethylene		<0.05	<0.05				
cis-1,3-pentadiene		<0.05	<0.05				
methyl parathion	0.060	0.15 (2)	0.58 (10)		1.04 (17)	0.56 (10)	0.15 (2)
p-nitroacetophenone		<0.05	<0.05				
p-nitroanisole	1.0	1.2 (1.2)	1.3 (1.3)				1.1 (1.1)
nitrobenzene	<0.1	<0.1	<0.1				
MTB	8.8	7.9 (0.90)	7.0 (0.79)			5.4 (0.62)	2.2 (0.25)

[a] Ratio of algae to distilled water results in parentheses. [b] Mean of three determinations is reported, standard deviation is typically < +20% of mean value.

constants, $(k_p)_p$, were computed from the initial, $[P]_0$, and final concentrations, [P], of substrate in the algae suspensions and in distilled water, assuming that the reactions were described by the following first-order rate expression:

$$\ln [P]_0/[P] = (k_p)_p t \quad (1)$$

First-order rate constants, $(k_p)_{act}$, were similarily computed for the PNA photoreactions.

Dark controls showed no transformations during the period of time used for the sunlight exposures.

Kinetic Studies Involving Anilines and Parathions. A series of aniline solutions ranging in concentration from 6.0×10^{-6} to 8.0×10^{-4} M were prepared. Each of these solutions was mixed with an equal portion of a suspension of *Chlamydomonas* sp. that had been washed with distilled water. The resulting suspensions were added to reaction cells that were irradiated in parallel in a photochemical merry-go-round (*18*) with light from a mercury lamp that was filtered through Corning 0-52 glass filters to block wavelengths less than 340 nm. Periodically, the reaction cells were removed and centrifuged, and the supernatants were analyzed for aniline by HPLC. Studies using the same aniline–*Chlamydomonas* suspensions were also conducted in sunlight for comparison, as described in the Screening Procedures section. Additional experiments were carried out by employing a constant aniline or methyl parathion concentration but with a varying concentration of algae. Other experiments involving algae treated by washing with ascorbic acid or by heat-killing were performed by simultaneously exposing to sunlight equivalent concentrations of the treated and the untreated algae suspended in aqueous solutions of aniline or methyl parathion.

Results and Discussion

Screening Studies. To determine the susceptibility of a variety of chemicals to algal transformation, screening studies were conducted by exposing aqueous suspensions of living algae containing chemicals at trace concentrations (less than 20 μM) to sunlight. Most of the chemicals selected for these screening studies had been shown to be reactive in the presence of algae (*11*) or were known to be susceptible to photosensitized reactions in natural waters (*16*). Preliminary studies showed that the components of commonly used culture media were effective photosensitizers, so the screening studies were conducted with washed algae suspended in distilled water or phosphate buffers. The algae did not metabolize the chemicals in the dark during the period of light exposure, which was usually less than 4 h, indicating that rate constants for dark metabolism of the substrates were no larger than about 0.03 h^{-1}.

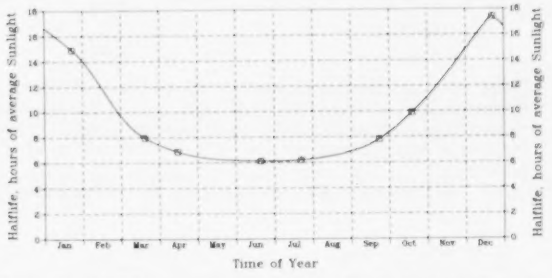


Figure 2. Half-lives computed for the direct photoreaction of *p*-nitroanisole in water exposed to sunlight at latitude 40° N (*19*, *20*).

Outdoor actinometers developed by Dulin and Mill (*19*) consisting of PNA in water were exposed to sunlight along with the algal suspensions. The rate constants for the algae-mediated photoreactions were ratioed to the first-order constants for the actinometer to correct for the variations in sunlight intensity (Table I). Whenever possible, rate constants were also obtained for competing photoreactions involving direct absorption of light. Rate constants for these direct photoreactions, also shown in Table I, are assumed to equal rate constants for photolysis of the chemicals in air-saturated, distilled water (*20*). Approximate half-lives for the algae-mediated and direct photoreactions can be computed by dividing the PNA half-lives shown in Figure 2 by the ratios in Table I. A representative value of $(k_p)_{act}$ for near the surface of a water body during summer in the U.S. is 0.11 h^{-1}.

Results, as shown in Table I, indicated that (1) most of the aromatic hydrocarbons examined reacted faster with algae present than in distilled water, (2) simple olefins were unreactive—isomerization and other reactions did not occur, (3) nitroaromatic compounds were not susceptible to algal phototransformation, with the exception of the organophosphorus insecticide methyl parathion, (4) the chlorinated cyclodiene insecticide aldrin was readily transformed by all the algae included in the study, (5) aniline was found to be the most reactive chemical with algae present, although its reactivity varied considerably from one alga to another, but phenol, another electron-rich benzene derivative, was at least an order of magnitude less reactive than aniline, (6) the direct photoreaction of MTB, a UV-absorbing compound that we previously used to quantitate light attenuation by sediments (*1*), was retarded

Table II. Kinetic Parameters for Transformation of Selected Organophosphorus Compounds in Suspensions of *Chlorogonium* sp. Exposed to Sunlight

compound	$(k_p)_p/(k_p)_{act}$[a]	chl *a* concn mg/L	ratio of algae to distilled H_2O	K_{ow}[b]
methyl parathion	0.58	6.8	10	2100
	0.53	6.8	8.8	
	0.39	6.3	6.5	
	0.16	1.8	2.7	
	0.10	0.68	1.7	
	0.06	0.0068	1.0	
	0.06[c]	0[c]		
parathion	1.6	6.8	27	6500
	0.06	0		
fenitrothion	1.38	1.7	1.0	2400
	1.33	0		
Ronnel	0.66	2.9	22	76000
	0.03	0		
chlorpyrifos	<0.1	2.2	<2	130000
	0.04	0		
diazinon	<0.1	2.4		
	<0.1	0		
malathion	0.5	7.8	>25	
	<0.02	0		
MTB	7.4	8.4	0.8[d]	
	9.2	0		

[a] Mean of three determinations is reported, standard deviation is typically ±15% of mean value. [b] Octanol–water partition coefficients (*23*): the methyl parathion value was determined by Lu and Metcalf (*27*). [c] Same value observed in distilled water and supernatant of centrifuged algal suspension. [d] Assumed to involve light attenuation only.

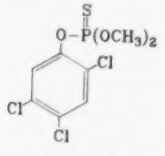
Table III. Influence of *Chlamydomonas* sp. on Rate Constants for Sunlight-Induced Reactions of Anilines (8.0×10^{-4} M)

substrate	medium	condition of algae	algae concn, mg/L Chl *a*	$(k_p)_p/(k_p)_{act}$[a]	K_{ow}[b]
aniline	algae suspension	growing in log phase	6.6	5.0	9.5
			0.65	0.55	
			0.06	0.089	
	supernatant from centrifuged, living algae suspension	not applicable	0	0.1	
	supernatant from centrifuged, heat-killed algae suspension	not applicable	0	1.2	
	distilled water	not applicable	0	0.04	
m-toluidine	algae suspension	growing in log phase	6.6	11	25
	distilled water	not applicable	0	<0.1	
p-chloraniline	algae suspension	growing in log phase	14	14	
	distilled water	not applicable	0	16	

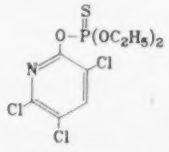
[a] Mean of three determinations is reported; standard deviation is typically ±15% of mean value. [b] Octanol–water partition coefficients from ref 21.

only slightly with the algae present, indicating that light attenuation did not have a major effect on the rates of the other reactions that were considered in Tables I and II.

Prompted by the methyl parathion results in Table I, additional organophosphorus chemicals were studied in the presence of *Chlorogonium* sp., a green alga (Table II). Several of the compounds exhibited enhanced reaction rates in the presence of the algae, although the aza aromatics were notably unreactive. For example, Ronnel and Chlorpyrifos have similar structures with the exception of



Ronnel



Chlorpyrifos

a nitrogen atom in the aromatic ring of the latter, but chlorpyrifos was much less reactive.

The combined results in Tables I and II indicate that the algae considered here do enhance the photolysis rates of organic chemicals, but in a very selective manner. These results prompted additional experiments that were designed to provide a better understanding of the algal-induced photoreactions.

Kinetic Model. The reactions of anilines and parathions were studied in some detail to obtain the data necessary to develop a kinetic model. The kinetic data for the *Chlamydomonas*-induced reaction of aniline could be described by a hyperbolic relation. (*A* and *B* are constants in the equation on Figure 3). At the low concentrations used in the screening studies reported in Tables I and II, the rate becomes approximately proportional to substrate concentration, and the kinetic data are described by a first-order rate expression. Other studies indicated that the rate constants for the algal-induced photoreactions of methyl parathion (Table II) and aniline (Table III) in sunlight are proportional to the algae concentration. The dependence of the rate constants on algal concentration could be described by eq 2, where k_d is the first-order rate

$$(k_p)_p = k_d + k_{alg}C_a \qquad (2)$$

constant for direct photolysis, k_{alg} is the second-order rate constant for the algal-induced photoreaction, and C_a is the algae concentration (mg of chlorophyll *a*/L). Applying a

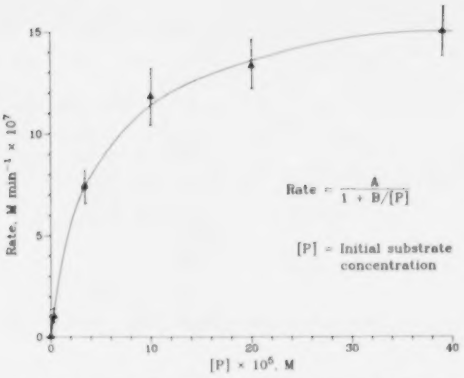


Figure 3. Dependence of initial rate for *Chlamydomonas*-induced photoreaction of aniline on substrate concentration; error bars denote the range of two replicate experiments.

linear least-squares fit to the kinetic data, we compute that values of k_{alg}, ratioed to the actinometer rate constants, are 0.068 ± 0.007 L/(mg of chlorophyll *a*) for the methyl parathion–*Chlorogonium* photoreaction and 0.75 ± 0.002 L/(mg of chlorophyll *a*) for the aniline–*Chlamydomonas* reaction.

Although both aniline and methyl parathion were found to be over 95% dissolved in the bulk water under the conditions employed for these studies, several experiments indicated that the observed reactions mainly involve substrate sorbed on the algae. First, the hyperbolic rate expression found for the aniline reaction (Figure 3) is consistent with a mechanism involving photoreaction of a reversibly sorbed substrate. Second, removal of the suspended algae by centrifugation greatly reduced the photolysis rate constants (Tables II and III). These experiments, however, did not exclude the possibility that the reactions involve transient, reactive oxidizing species that were released by the algae into the bulk water upon irradiation. Finally, the ratio of the rate constants for algal-induced photoreaction of parathion to methyl parathion, 2.8, approximately equalled the ratio of their octanol–water partition coefficients, 3.1 (Table II). In comparison, direct photolysis rates of these chemicals were the same (Table II). Likewise, the ratio of rate constants for *m*-toluidine and aniline, 2.2, was close to the ratio of their K_{ow}'s, 2.6 (Table III). Recent studies by Geyer et al. (*22*) have indicated that sorption of nonionic, organic chemicals by algae is inversely correlated to their water solubilities. Because it is well established that water solubility is inversely correlated with K_{ow} (*23*), it follows that the results described above are also consistent with a kinetic model that includes sorption of the substrate on the algae prior to photoreaction.

Although the removal of the *Chlamydomonas* by centrifugation greatly decreased the photolysis rate of aniline, photolysis of the aniline in sunlight was still more rapid in the supernatant than in distilled water (Table III). When the *Chlamydomonas* cells were heat-killed, they released substances into the bulk water that caused rapid photolysis of the aniline in sunlight (Table III). These results are consistent with other recent studies by Momzikoff and co-workers (*24*) and by Matsumura and Esaac (*25*), who have shown that substances released by algae can photosensitize a variety of reactions in water.

A kinetic model that accounts for the results discussed above is shown in Figure 4. The algae–substrate reaction is proposed to involve reversible sorption of the substrate by the algae, where photosensitizing substances are present. As the substrate concentration is increased, the re-

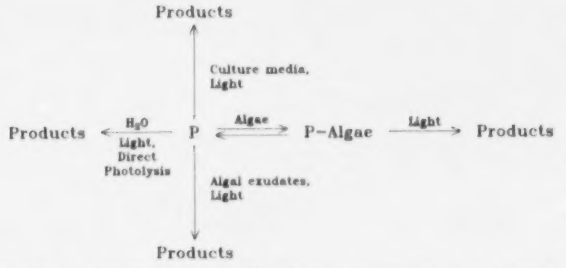


Figure 4. Kinetic model for light-induced transformation of substrate involving algae; P and P-algae represent substrate dissolved in bulk water and sorbed on the algae, respectively.

active sites on and/or in the algae become saturated, and the rate becomes independent of substrate concentration. The model is consistent with the general finding that the algae have the least effect on photolysis rates of chemicals that rapidly undergo direct photolysis, a competing process. For example, the photolysis rate constants of fenitrothion and *p*-chloraniline in sunlight are almost unaffected by the presence of algae (Tables II and III). Finally, the reaction scheme takes into account the findings that algal exudates or culture media photosensitize reactions. The effects of culture media may involve, in part, free-radical reactions that are initiated by photolysis of media constituents. For example, Skurlatov et al. (*26*) have found that the ferric–EDTA complex, a species commonly added to algal culture media (*13*), rapidly photosensitizes the reaction of methyl parathion in sunlight.

The kinetic model may be used in conjunction with the data in Tables II and III to estimate the photoreactivity of various substrates when sorbed by the algae. Assuming that the concentration ratio of sorbed to dissolved substrate is constant throughout the reaction, the rate constant for photoreaction of the sorbed substrate equals $(k_p)_p$ divided by the fraction of total substrate that is sorbed. For methyl parathion and parathion, the fractions sorbed at a *Chlorogonium* concentration of 6.8 mg of chlorophyll *a*/L were 0.023 and 0.071, respectively. Employing the kinetic data for this concentration (Table II) and assuming a value of 0.11 h^{-1} for $(k_p)_{act}$ (Figure 2), the rate constant for photoreaction of the sorbed parathions in sunlight was computed to be about 2.6 h^{-1}. This value is about 390 times larger than the rate constant for direct photolysis of these substrates in water. With aniline and *m*-toluidine the fraction sorbed was less than 1%, indicating that the rate constant for photoreaction of the sorbed anilines is greater than 55 h^{-1} based on kinetic data in Table III. Thus, the anilines are estimated to be over 12000 times more reactive when sorbed to *Chlamydomonas* sp. than when dissolved in water.

Nature of Algal-Mediated Photoreactions. Experiments were conducted to elucidate the mechanisms of the algal transformations, thus providing some basis for generalizing the results of this study.

Several experiments indicated that the photosynthetic apparatus of two green algae did not play a role in the sunlight-induced transformations of aniline or methyl parathion. Prolonged irradiation of the algal suspensions using monochromatic light at a wavelength (665 nm) that corresponds to peak light absorption by the chlorophyll in the algae (*3*) resulted in no reaction of either substrate. Moreover, the rate constants for photoreaction of methyl parathion or aniline were unaffected by heat-killing (50 °C for 0.5 h) the algae (Table IV). The heat-killed algae were washed by distilled water prior to the irradiations to remove the sensitizing substances that were released into the bulk water. Similar results have also been reported

Table IV. Kinetic Parameters for Sunlight-Induced Photoreactions of Methyl Parathion and Aniline with Algae Present

substrate	algae	treatment	algae concn, mg/L[a]	$(k_p)_p/(k_p)_{act}$[b]
methyl parathion	*Chlorogonium* sp. (no. 1)	none	530	0.28 ± 0.03
		heat-killed	530	0.26 ± 0.02
		washed with ascorbic acid	530	0.26 ± 0.02
	none present			0.06
aniline	*Chlamydomonas* sp.	none	160	2.7 ± 0.2
		heat-killed	160	3.1 ± 0.1
		washed with ascorbic acid		
	none present			0.04

[a] Computed from chlorophyll *a* concentration of algae prior to treatment assuming algal dry weight is 67 times greater than chlorophyll weight (*16*). [b] Mean values of three experiments are reported.

by Matsumura and Esaac (*25*), who found blue-green algae photosensitized reactions of several pesticides more rapidly when the algae were denatured by boiling.

The stability of the algai-associated sensitizers to heat, coupled with the fact that hydrous iron oxides known to be photochemically active (*26*) adsorb on algal cells from growth media (*14*), prompted us to examine the possibility that ferric hydroxide sorbed to the algae was the sensitizing agent. Employing a procedure similar to one described by Anderson and Morel (*14*), we washed the algae with an acidic solution of ascorbic acid to remove cell-associated ferric hydroxide. As shown in Table IV, this washing procedure had no effect on the rate constants for the photoreactions, excluding the possible involvement of hydrous iron oxides.

Conclusions

The results of this study unequivocally demonstrate that a variety of algae can accelerate the sunlight-induced transformations of nonionic organic chemicals, although in a very selective fashion. Components of culture media as well as substances released by the algae into the bulk water are also capable of photosensitizing reactions. The effects of the latter were minimized in this study by washing the algae with distilled water prior to irradiation. Dark metabolism of the organic substrates by the algae studied here was found to make little or no contribution to the observed transformations.

Detailed kinetic and product studies of the reactions of the anilines and parathions lead to several conclusions. The algal-induced reactions involve the reversible sorption of the substrate by the algal cells, where photosensitizing substances are present. At low substrate concentrations the reaction rates are first order with respect to both algae and substrate concentrations. Employing the rate expression and typical algae concentrations that are found in natural freshwaters, which are several orders of magnitude lower than used in this study, we conclude that light-induced algal transformation of most of the 22 chemicals studied here would have very little effect on their concentrations in lakes and rivers. Competing processes such as direct photolysis are more rapid. On the other hand, the rates are subject to a hydrophobic effect, suggesting that algal-induced photoreactions of pollutants more hydrophobic than the ones included in this study may be much more rapid. Indeed, rate constants computed for sunlight-induced photoreaction of substrates sorbed by the algae were remarkably large, ranging from an estimated near-surface average of 2.6 h^{-1} for sorbed parathion to over 55 h^{-1} for sorbed aniline.

Elucidation of the identity of the algal-associated photosensitizers was beyond the scope of this study. It was shown, however, that the rate constants for reactions of anilines and parathions were unaffected by heat-killing the algae and that the use of 665-nm light to sensitize the reactions was very inefficient. These results indicate that the photosynthetic apparatus of the algae was probably not involved in the algal transformations studied here.

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Supplementary Material Available

Molecular structures of the synthetic chemicals included in this study and a first-order kinetic plot of the data for the *Chlamydomonas*-induced photoreaction of aniline (4 pages) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper or microfiche (105 × 148 mm, 24× reduction, negatives) may be obtained from Distribution Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, DC 20036. Full bibliographic citation (journal, title of article, author, page number) and prepayment, check or money order for $7.50 for photocopy ($9.50 foreign) or $6.00 for microfiche ($7.00 foreign), are required.

Registry No. MTB, 79049-96-0; pyrene, 129-00-0; phenanthrene, 85-01-8; fluoranthene, 206-44-0; naphthalene, 91-20-3; aniline, 62-53-3; phenol, 108-95-2; aldrin, 309-00-2; *cis*-1,2-dichloroethylene, 156-59-2; *cis*-1,3-pentadiene, 1574-41-0; methyl parathion, 298-00-0; *p*-nitroacetophenone, 100-19-6; *p*-nitroanisole, 100-17-4; nitrobenzene, 98-95-3; parathion, 56-38-2; fenitrothion, 122-14-5; ronnel, 299-84-3; chlorpyrifos, 2921-88-2; diazinon, 333-41-5; malathion, 121-75-5; *m*-toluidine, 108-44-1; *p*-chloroaniline, 106-47-8.

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